Ash related challenges from a boiler manufacturer’s point of view

Chemistry in energy technology 2020
Sonja Enestam / Hanna Kinnunen
Contents

• Valmet Technologies

• Fuels
  – Trends
  – Challenges

• Ash related challenges
  – Bed agglomeration
  – Fouling and slagging
  – Corrosion

• The significance of corrosion

• How do we tackle issues of corrosion?
  - Questions and technical solutions

• Recent trends and activities
  – Ash handling and utilization
• Leading supplier of process technologies, automation and services for the pulp, paper and energy industries
Our offering by business line

**Paper**
- Recycled fiber lines
- Tailor-made board and paper machines
- Modularized board and paper machines
- Tissue production lines
- Modernizations and grade conversions
- Standalone products

**Pulp and Energy**
- Complete pulp mills
- Sections and solutions for pulp production
- Multifuel boilers
- Biomass and waste gasification
- Emission control systems
- Biotechnology solutions e.g. for producing bio fuels

**Services**
- Spare parts and consumables
- Paper machine clothing and filter fabrics
- Rolls and workshop services
- Mill and plant improvements
- Maintenance outsourcing
- Services energy and environmental solutions

**Automation**
- Distributed control systems
- Quality control systems
- Analyzers and measurements
- Performance solutions
- Process simulators
- Safety solutions
- Industrial Internet solutions

Focus in customer benefits
Total energy consumption in Finland by source

Source: Statistics Finland, Energy supply and consumption
Renewable energy sources 1970–2018

Source: Statistics Finland, Energy supply and consumption
Boiler product family

BFB boilers

CFB boilers

Recovery boilers

Dust burner boilers

CFB Gasifier

Oil & Gas Boilers
BFB main components
Valmet BFB combustion technology

https://www.youtube.com/watch?v=KcR62W2z8KE
CFB main components

- Drum
- Furnace
- Loop seal
- Fluidizing grid
- Cyclone
- Convection pass
- Final superheater
Valmet CFB combustion technology

https://www.youtube.com/watch?v=4bOpZcT0CuE
Fluidized Bed Combustion Technology
The fuel flexible solution

- Over 75 CFB boilers since 1980
- Capacity range 30–350 MWₑ

CFB
• Fuel moisture range 0 - 60 %
• High steam parameters for corrosive fuels
• Low Emissions
• Coal co-combustion and backup

- High boiler efficiency
- >99.5% carbon burnout with low excess air
- Low Emissions
- Fuel Flexibility
- High Reliability, typical >98 %

BFB
• Fuel moisture range 25 – 65 %
• Steam parameters depending on fuel
• Low Emissions
• Full capacity with oil and gas

Almost 200 BFB boilers since 1974
Capacity range 10–100 MWₑ
Towards CO$_2$ neutral fuels

- Sustainable energy
- Fossil
- Recycled fuels
  Cl, K, Na, Pb, Zn, ash
- Wood pellets
  Price
- Agro
  Cl, K, P, Si
- Woody bio
  Cl, K, ash
Parameters steering the fuel choice
Balancing economy and sustainability

Environmental regulations
- CO₂ trade
- green energy benefits

Ethical aspects

Fuel availability

Price

Fuel quality and combustibility
- emissions
- corrosion
- ash quality
- bed sintering

Economy
The fuel dilemma

- **Fossil**
  - Hard coal

- **Wood biomass**
  - Northern wood
  - Pulp&Paper sludges
  - Wood pellets

- **Fast growing wood**
  - Willow
  - Eucalyptus

- **Agro biomass**
  - Straw
  - Sunflower hulls
  - Corn Stover
  - Miscanthus

- **Recycled fuels**
  - Packaging waste
  - Recycled wood
Fuel properties

- Heating value
- Moisture
- Physical characteristics
- Ash content
- Ash composition
  - Cl, S, Ca, K, Na, Pb, Zn, P…

Furnace dimensions
- Air / fuel ratio
- Use of flue gas recirculation

Fuel feeding
- HSE

Fouling and slagging propensity
- Ash handling

Fouling propensity
- Corrosivity
- Bed agglomeration
- Emissions
- Ash quality
The role of chemistry in a heat and power plant
The influence of fuel composition on the combustibility

Low melting ash

Corrosive environment

Fouling

Corrosion

Slagging

Bed sintering

S

Ca

Pb^{2+}

Zn^{2+}

Cl^-

K^+

Na^+

Cl^-

K^+

Na^+

Ca
Typical analyses of different types of fuels
minimum – **average** – maximum

<table>
<thead>
<tr>
<th>Moisture</th>
<th>Peat</th>
<th>Wood chips</th>
<th>Bark</th>
<th>Demolition wood</th>
<th>SRF</th>
<th>AGRO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (815°C) [wt-% of ds]</td>
<td>2 – 6 – 18</td>
<td>0.2 – 1.5 – 4</td>
<td>0.1 – 4.0 – 13</td>
<td>1 – 3.5 – 13</td>
<td><strong>10 – 18 – 26</strong></td>
<td>4 – 6.5 – 12</td>
</tr>
<tr>
<td>HHV&lt;sub&gt;dry&lt;/sub&gt; [MJ/kg]</td>
<td>17 – 22 – 23</td>
<td>19 – 21 – 26</td>
<td>15.5 – 20 – 33</td>
<td>18 – 19.5 – 21</td>
<td>15.0 – 19.5 – 25</td>
<td>16.5 – 18.5 – 19</td>
</tr>
<tr>
<td>S [wt-% of ds]</td>
<td>0.1 – 0.2 – 0.8</td>
<td>0.01 – 0.04 – 0.09</td>
<td>0.01 – 0.05 – 0.2</td>
<td>0.01 – 0.07 – 0.15</td>
<td>0.1 – 0.5 – 0.7</td>
<td>&lt;0.08 – 0.08 – 0.2</td>
</tr>
<tr>
<td>Cl [wt-% of ds]</td>
<td>0.02 – 0.04 – 0.25</td>
<td>&lt;0.01 – 0.01 – 0.01</td>
<td>&lt;0.01 – 0.07 – 0.3</td>
<td>0.01 – 0.07 – 0.26</td>
<td><strong>0.2 – 0.7 – 1.6</strong></td>
<td>0.15 – 0.3 – 1</td>
</tr>
<tr>
<td>Pb [mg/kg of ds]</td>
<td>2 – 8 – 30</td>
<td>&lt;5</td>
<td>1 – 10 – 30</td>
<td><strong>10 – 150 – 650</strong></td>
<td>1 – 50 – 110</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>
Agglomeration
Agglomeration mechanism

fuel = green circles
ash = red circles
sand = grey shapes
Agglomeration mechanism

- Bed particle (B)
- Sticky material (A) consists mostly of K, Ca, Si, Na
- The melting temperature of the sticky material is < 800 °C
Bed Agglomeration -> solutions

- Bed temperature: < 750 °C
- Bed material removal
- Additives, e.g. kaolin
- Inert (quartz-free) bed material
Slagging and fouling
Fouling & slagging
Influence of fuel composition and process conditions on slagging and fouling

- Amount of ash in the fuel and composition of the ash
  - Ash melting behavior => stickiness of the ash
  - Condensable matter

- Increased temperature => increased slagging and fouling, often caused by increased load

- Often leads to a "snow ball" effect progressing with the flue gas flow in the boiler

- Swirls caused by the air feeding system can cause areas with high slagging in the furnace
  - CFD modelling

- The fuel feeding system in combination with the air feeding can move the combustion too high up in the furnace
  - Both systems can be optimized with CFD modelling
Effects of slagging and fouling

- Big pieces of slag falling down can lead to defluidization of the bed
- Reduced heat transfer => Decreased efficiency of the boiler
- Increased need for sootblowing (steam consumption)
- Increased corrosion risk
  - Without deposits usually no corrosion
  - All deposits are not corrosive
- Plugging of the boiler
  - Unavailability
- Partial plugging leads to increased flow velocity which in turn leads to erosion
  - Tube leakages
  - Unavailability
Avoiding slagging and fouling

- Correct boiler design based on the fuel properties
  - Empty pass in waste boilers
  - Correct placement on heat exchangers
  - Tube spacing of heat exchangers
- Understanding of fuel ash properties
  - Avoiding difficult fuel mixtures at high loads
  - Avoiding certain fuels
- Limiting the furnace temperature
  - By recirculating flue gas
- Furnace cleaning
  - Avoiding the snow ball effect
- Optimization of sootblowing
  - Sufficient amount of superheaters
  - Right type of superheaters
  - Sufficient soot blowing, 1/d -> 1/ shift
- Boiler cleaning at annual shut down
Corrosion
The influence of corrosion on boiler technology and plant efficiency

- Final steam temperature and pressure → Efficiency
- Change of material → Price
- Fuel mixture and boiler availability → Economy
- Superheater placement → Design

The diagram illustrates various aspects of boiler technology and their impact on efficiency and design.
Corrosion types and mechanisms in BFB and CFB boilers
Different corrosion types – BFB boilers

- Alkali chloride induced corrosion
- Heavy metal induced corrosion
- Erosion-corrosion
- Dew point/low temperature corrosion
Different corrosion types – CFB boilers

- Erosion-corrosion
- Alkali chloride induced corrosion
- Heavy metal chloride induced corrosion
- Dew point / low temperature corrosion
- Alkali chloride induced corrosion
Corrosion types and mechanisms

Alkali chloride induced corrosion; well understood and established solutions

- Condensation of KCl(g)
- KCl reacts with the metal
- Critical temperature range: material temperature > 450 °C

Alkali chloride induced corrosion of the hottest superheaters
➢ Bio and waste combustion
Corrosion types and mechanisms

Heavy metal induced corrosion; the main research topic during the last 10 years

Heavy metal induced corrosion of cooler heating surfaces such as primary superheaters and furnace walls

➢ Waste combustion
The influence of deposit composition on ash melting behavior

![Graph showing the melting behavior of different compositions at varying temperatures.]

- **Alkali salt (Na,K,SO₄,Cl)**
- **Alkali salt + PbCl₂**
- **Alkali salt + ZnCl₂**

Amount of melt [wt%] vs. Temperature [°C]
Pb induced corrosion
Combustion of waste wood

Formation of corrosive compounds: KPb$_2$Cl$_5$ and K$_2$PbCl$_4$

Pb present mostly as chlorides

Fuel:
High concentrations of Pb + Cl

Corrosion mechanism:
Formation of FeCl$_2$ (with low alloy steel)
Low temperature corrosion
Old problem – new understanding of the mechanism

Corrosion of air preheaters caused by hygroscopic salts
➢ Bio and waste combustion

- Hygroscopic chlorides in deposits
- Critical temperature range: ~100-140 °C

Herzog, T.; Müller, W.; Spiegel, W.; Brell, J.; Möller, D.; Schneider, D (2012)
Corrosion types and mechanisms in recovery boilers
Location of corrosion in recovery boilers

Upper furnace:
- Superheaters
- Superheater ties

Lower furnace:
- Bottom tubes
- Wall tubes
- Air ports

Alkali chloride induced corrosion

Sulphidation

Second pass:
- Boiler bank
- Economizers

Acidic sulphates
Recovery boiler: Carryover particles on tube surface

- Locally reducing atmosphere
- Risk for molten phase corrosion
Molten phase corrosion

- Molten deposit on the tube surface
- Better contact with tube surface
- Faster reaction
- Catastrophic corrosion rates
- Occurs when $T_{\text{mat}} > T_0$ of the deposit
- Rule of thumb: $T_{\text{mat}} < T_0$
The influence of melt formation in the deposit

Steel: T91
Time: 168 h

The thickness of the oxide, μm

No Ash
Ash 5, $T_0=884\, ^\circ C$
Ash 6, $T_0=834\, ^\circ C$
Ash 7, $T_0=625\, ^\circ C$
Ash 8, $T_0=526\, ^\circ C$
Ash 9, $T_0=621\, ^\circ C$
Ash 10, $T_0=522\, ^\circ C$
Technical solutions
From fuel to stack
Understanding the phenomena

- Fuel
- Air
- Combustion reactions
- Temperature
- Gas atmosphere
- Ash
- Deposit
- Material
- Corrosion products
- Emissions
- Ash utilization

- $\text{K}_2\text{SO}_4$
- $\text{Na}_2\text{SO}_4$
- KCl
- NaCl
- ZnCl$_2$
- PbCl$_2$
The corrosion rate is influenced by:

- Steel grade
- Material temperature
- The corrosivity of the environment
  - Flue gas composition
  - Flue gas temperature
  - Solid and/or molten fly ash
  - Deposit composition
Corrosion -> solutions

1. Superheater material and coatings
2. Steam temperature
3. Tube shields – most corrosive locations
4. Superheater location
5. Superheater design
6. Fuel mixture: Co-firing or additives
7. Gasification
Tube shields

Most corrosive locations
Superheater location

Reduced concentration of gaseous, corrosive chloride in the vicinity of tube surfaces
Ways to minimize corrosion
Modification of the combustion environment

• Additives
  ➢ Sulphur
  ➢ Aluminium sulfate $\text{Al}_2(\text{SO}_4)_3$
  ➢ Ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$
  ➢ Ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$

• Co-combustion
  ➢ Peat
  ➢ Coal
  ➢ Sludge
Corrosion management by sulphur addition

- The sulphate eliminates alkali chlorides in the gas phase and attaches to superheater surfaces forming a protective coat and neutralize the effects of alkalichloride in the process.
- Sulfate decomposes at high temperature:
  \[
  \text{Fe}_2(\text{SO}_4)_3 \rightarrow 2 \text{Fe}^{3+} + 3 \text{SO}_4^{2-}
  \]
- Alkali chloride reacts with sulfur trioxide or dioxide
  \[
  2\text{MCl} (g,c) + \text{SO}_3 (g) + \text{H}_2\text{O} (g) \rightarrow \text{M}_2\text{SO}_4 (g,c) + 2 \text{HCl} (g)
  \]
  \[
  2\text{MCl} (g,c) + \text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) + \text{H}_2\text{O} (g) \rightarrow \text{M}_2\text{SO}_4 (g,c) + 2 \text{HCl} (g)
  \]
where M is Na or K.

Slow down corrosion of superheaters
The influence of fuel mixture on corrosion

Corrosive bio fuel mixture requires stainless steel in the hottest superheaters.

Adding sulphur rich fuel (e.g. peat) or S-additive enables the use of low alloy superheater material.
Gasification

Recycled waste gasification plant for Lahti Energia Oy

→ Valmet delivery: waste gasification process, gas boiler, flue gas cleaning system with auxiliary and automation systems

→ 2 gasification lines: 50 MW of electricity and 90 MW of district heat

→ High-efficiency (gas boiler 121 bar, 540 C) conversion of recycled waste to energy and reduction of fossil fuels

→ Waste is turned into combustible gas, which is cooled, cleaned and combusted in a high-efficiency gas boiler to produce steam for a steam turbine
Corrosion related plant optimization

- **Efficiency**
  - Maximize steam T and p

- **Availability**
  - Minimize shut-downs due to corrosion, fouling or bed sintering

- **Maintenance costs**
  - Minimize the need for tube replacement (=minimize corrosion)

- **Investment costs**
  - Optimize material choice (Good enough material but not too good)
Corrosion control is a piece of a big puzzle of economics.

- Investment cost
- Plant efficiency
- Plant availability
- Maintenance costs
- Fuel cost
- Fuel quality
- Power value
- Plant profitability

Corrosion control

Plant profitability
Ash handling and utilization
Ash formation

- Fuel
- Bed material
- Additives: Sulphur, Sulphates, Ammonia, Urea
- Temperature profile
- Residence times
- Air/oxygen levels

- Additives: Sodium bicarbonate, Calcium hydroxide, Activated carbon

- Bottom ash
- Fly ash
- Fly ash from BHF/ESP
- Scrubber
Ash formation – fluidized bed combustion

Bottom ash

- Particles that are too coarse for fluidizing
  - oversized sand
  - stones
  - other pollutants/metallic particles in the fuel
- Removal through the furnace bottom and transportation to the bottom ash container
- Bottom ash produced ~5-10 % (FB combustion)

**Utilization:**
Road construction or other landscaping (low nutrient content and limited leaching)
Ash formation – fluidized bed combustion

Fly ash

- Majority of the ash formed is fly ash
- Fly ash produced ~90-95 % (FB combustion)

→ Major challenges will arise relating to the ash management, further utilization more complex than with bottom ash
→ The primary concerns are ash storage, disposal, usage and the presence of unburned carbon
Ash quality and utilization

- > 1.3 ton ash produced in Finland annually, of this 500 000–600 000 ton is from biomass and peat combustion
- Ash can be further utilized e.g.
  - As fertilizers
  - asphalt filling material, in road works and excavation
  - In concrete and cement industry
- Ash utilization principle is that it shall not be a risk for human health or environment
- Limits defined by legislation and authorities
- Ash quality is defined by e.g. elemental composition, leachability and pH. Depends on fuel composition, fuel mixtures, combustion technology and conditions, additives, flue gas cleaning technology and additives
- The most critical component of ash from woody biomass is typically Cd
- Most common use in Finland at the moment are excavation and forest fertilizing
- Disposal cost, valuable nutrient and metals and sustainability issues are driving forces for active research in ash utilization
  - Stabilization of dredging soil
  - Fertilizers
  - Geo-polymers
  - Cement and concrete production
  - Use in water purification and composting
Residues from waste incineration

Fig. 2. Management of APC residues from MSW incineration.

BA: Bottom ash
FA: Fly ash
ESP: Electrostatic precipitator ash
FF: Fabric filter or Baghouse ash
DS, SDS, WS: dry or wet scrubbing residues
CA: Cyclone ash

In Finland ~45000 ton APC/fly ash formed annually

Ref.: D. Lindberg / Aalto University / International Process Metallurgy Symposium on ash treatment methods (http://ipms2019.aalto.fi/)
Replacement of fossil fuels with CO$_2$ neutral fuels in Asia
Agricultural residues in AP

- Increased awareness of sustainability issues
- Pressure to decrease the use of coal => increase use of renewable fuels
- Lack of forest based biomass => interest in biobased residues and waste utilization
- Interesting fuels e.g. residues from palm oil mills and straw
- Typically high in potassium and chlorine

<table>
<thead>
<tr>
<th>Challenge</th>
<th>Severity</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temperature corrosion</td>
<td>Moderate</td>
</tr>
<tr>
<td>Mid temperature corrosion</td>
<td>Minor</td>
</tr>
<tr>
<td>Fouling &amp; slagging</td>
<td>Severe</td>
</tr>
<tr>
<td>Bed agglomeration</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
Oil palm:

Empty Fruit Bunches - EFB

Palm Kernel Shell - PKS

EFB fibers

Ref: http://suaraindonesia-news.com
Main takeaways

- Energy from biomass = utilization of waste streams
- Challenging fuels to burn efficiently with high availability
  - Pay attention to Cl, K, Na, S, Ca, Pb
- Main technical challenges
  - Bed agglomeration
  - Fouling
  - Corrosion
- Ash utilization
  - Disposal cost, valuable nutrient and metals and sustainability issues are driving forces for active research
- Challenges can be handled through understanding of combustion chemistry